CCLXI.—*Chlorocamphoranilic Acids and Camphorochlorophenylimides.*

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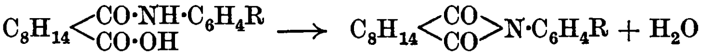
IN a previous communication (J., 1925, **127**, 1966) it was shown that the reaction



$$C_8H_{14}<\begin{matrix}CO\cdot NH\cdot C_6H_4R\\ CO\cdot OH\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CO\\ CO\end{matrix}>N\cdot C_6H_4R + H_2O$$

is dependent on the nature of the group R and other factors, the stability of the acid increasing as R becomes more negative. The carboxycamphoranilic acids (*loc. cit.*) produced by the condensation of camphoric anhydride with aminobenzoic acids are very stable and have not been converted into camphorimides.

The reactions of camphoric anhydride with *o*-, *m*-, and *p*-chloroanilines have now been investigated. The object was to examine the effect of decrease in the negativity of R(CO_2H to Cl) on the above reaction. As expected, the condensation products yielded a mixture of chlorocamphoranilic acids and camphorimide derivatives, thus showing that with the decrease in the negativity of the group there is a tendency towards the formation of ring compounds. The position of the substituent seems to have some effect on the yield of the camphorimide, which is about 20% in the case of the para-derivative and 5 to 6% in the case of the ortho- and meta-derivative. This question is being fully investigated in the condensation products of camphoric anhydride and bromoanilines and iodoanilines.

Wootton (J., 1910, **97**, 405) also has condensed camphoric anhydride with chloroanilines. The melting points of his acids are lower than ours, because they contain the corresponding camphorimides formed in the condensations.

With regard to the optical rotations of the chlorocamphoranilic acids, (*a*) the *o*-chloro-acid gives negative values in acetone and methyl ethyl ketone and positive values in methyl alcohol and ethyl alcohol; (*b*) the relation between the molecular rotation and the position of the chlorine atom is in all solvents $p > m > o$; (*c*) the molecular rotatory powers of these acids do not follow the order of the dielectric constants of the solvents used.

The following table gives the molecular rotatory powers of camphoranilic acid and some of its ortho-derivatives in methyl alcohol, ethyl alcohol, and acetone.

	$[M]_D$.		
	Methyl alcohol.	Ethyl alcohol.	Acetone.
H*	+150°	+131°	+101°
CO_2H	−584	−574	−551
CH_3*	+146	+144	+ 98
Cl	+ 57·8	+ 35·6	− 40·3

* Singh and Puri, J., 1926, 504.

The relative changes of rotatory power in methyl alcohol and acetone are given by $CO_2H > H > CH_3 > Cl$. This corresponds with the relative polarity of the groups as deduced from molecular inductive capacities (Rule, J., 1926, 553).

The molecular rotations of the *p*- and *m*-substituted camphorophenylimides are considerably lower than those of the corresponding acids, whereas in the case of the *o*-substituted derivatives they are of the same magnitude.

EXPERIMENTAL.

Condensation of Camphoric Anhydride with o-*Chloroaniline.*—Equimolecular quantities of these and a little fused sodium acetate were heated together at 145—150° for 4 hours. The product was dissolved in 90% alcohol, decolorised with animal charcoal, precipitated, and extracted with a dilute solution of sodium bicarbonate, which left a very small residue of camphoro-*o*-chlorophenylimide. This crystallised from alcohol in fine, light needles, m. p. 128° (Wootton, *loc. cit.*, gives m. p. 125—126°). It was soluble in acetone, methyl alcohol, and ether, but sparingly soluble in ethyl alcohol (Found : C, 65·6; H, 6·4; Cl, 12·2. Calc., for $C_{16}H_{18}O_2NCl$: C, 65·8; H, 6·2; Cl, 12·1%).

The bicarbonate solution was acidified and the amorphous solid obtained was recrystallised twice from 60% alcohol; it then melted at 165° (Wootton, *loc. cit.*, gives m. p. 139—140°, which is that of a mixture of 2′-chlorocamphoranilic acid and the imide). *2′-Chlorocamphoranilic acid* is soluble in acetone, methyl alcohol, and ethyl alcohol and moderately easily soluble in ether (Found : C, 62·2; H, 6·8; Cl, 11·2; equiv. by titration with NaOH, 311. $C_{16}H_{20}O_3NCl$ requires C, 62·0; H, 6·5; Cl, 11·5%; equiv., 309·5).

Condensation of Camphoric Anhydride with m-*Chloroaniline.*—The procedure was that described above. The alcoholic solution slowly deposited fine, silky needles of camphoro-*m*-chlorophenylimide, which melted at 176° after recrystallisation (Wootton gives m. p. 172—173°). It was soluble in acetone, methyl alcohol, and ether, and sparingly soluble in ethyl alcohol (Found : C, 66·0; H, 6·9; Cl, 12·2%).

The alcoholic filtrate, on being concentrated, gave a further crop of impure imide. The filtrate from this was poured into a large volume of water, and the precipitate of 3′-chlorocamphoranilic acid thus obtained was dissolved in dilute sodium bicarbonate solution, reprecipitated, and crystallised from 60% alcohol, the pure acid separating in thin plates, m. p. 216—217° (Wootton gives m. p. 207—209°). It was soluble in acetone, methyl alcohol, and ethyl alcohol, and very sparingly soluble in ether (Found : C, 61·8; H, 6·85; Cl, 11·9%, equiv., 304).

Condensation of Camphoric Anhydride with p-*Chloroaniline.*—The procedure was that described above, and the solvent absolute alcohol. The solution slowly deposited stout, prismatic needles of camphoro-*p*-chlorophenylimide, which were twice recrystallised from alcohol; they then melted at 165° (Wootton gives m. p. 162—163°). The imide is soluble in acetone, methyl alcohol and ether, and very sparingly soluble in ethyl alcohol (Found : C, 65·5; H, 6·5; Cl, 12·3%).

From the united filtrates a second crop of the imide was obtained, m. p. 164—165°, after recrystallisation from alcohol. 4′-Chlorocamphoranilic acid, isolated in the same way as the *m*-compound, crystallised from alcohol in needles, m. p. 197° (Wootton gives m. p. 192—194°). It was soluble in acetone, methyl alcohol and ethyl alcohol, and sparingly soluble in ether (Found : C, 61·7; H, 6·6; Cl, 11·9%; equiv., 314).

In all the condensations, complete separation of the acid from the imide could be effected by fractional crystallisation from ethyl alcohol, but it was a rather tedious process.

Molecular rotations of the chlorocamphoranilic acids and camphorochlorophenylimides.

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha]_D$.	$[M]_D$.
	2′-Chlorocamphoranilic acid.				
MeOH	0·4391	18°	+0·61°	+18·7°	+57·8°
EtOH	0·4444	,,	+0·41	+11·5	+35·6
Me$_2$CO....................	0·2654	,,	−0·28	−13·2	−40·8
MeEtCO..................	0·4210	,,	−0·29	− 8·6	−26·6
	3′-Chlorocamphoranilic acid.				
MeOH	0·1475	18	+0·62	+52·5	+162·4
EtOH	0·1384	,,	0·48	43·3	134·0
Me$_2$CO	0·1268	,,	0·32	31·5	97·5
MeEtCO..................	0·1306	,,	0·42	40·2	124·4

Solvent.	Conc. (g./25 c.c.).	Temp.	α_D.	$[\alpha_D]$.	$[M]_D$.
		4′-Chlorocamphoranilic acid.			
MeOH	0·1870	18°	+0·88	+58·8	+183·0
EtOH	0·1314	,,	0·54	51·3	158·7
Me_2CO	0·1493	,,	0·46	38·5	119·0
MeEtCO	0·1302	,,	0·51	48·9	150·3
		Camphoro-*o*-chlorophenylimide.			
MeOH	0·1522	25°	+0·16	+13·14	+38·3
EtOH	0·1592	,,	0·18	14·1	41·1
Me_2CO	0·2468	,,	0·24	12·1	35·2
MeEtCO	0·2348	,,	0·26	13·8	40·2
		Camphoro-*m*-chlorophenylimide.			
MeOH	0·2030	25°	+0·23	+14·16	+41·1
EtOH	0·2256	,,	0·25	13·8	40·2
		Camphoro-*p*-chlorophenylimide.			
MeOH	0·2014	25°	+0·32	+19·8	+51·7
EtOH	0·2589	,,	0·33	15·9	46·4
Me_2CO	0·2432	,,	0·28	14·3	41·7
MeEtCO	0·3326	,,	0·44	16·5	48·0

The readings were taken in a 2-dm. tube within ½ hour of making up the solution. There was no mutarotation.

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